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(54) Title: HOT SHAPING POLYHYDROXYALKANOATE POLYMERS

(57) Abstract

This invention relates to processes for producing a shaped object of polyhydroxyalkanoate (PHA) that makes it possible to omit the preliminary extrusion-compounding step, thus saving expense and limiting loss of molecular weight. The process comprises producing a biomass containing particles of PHA and non-PHA cell material (NPCM), separating the NPCM, suspending the PHA particles in water, agglomerating the suspended PHA particles to a suitable weight average particle diameter, separating the agglomerated PHA particles from the suspension, drying the agglomerated PHA particles, and hot shaping the dry, agglomerated PHA particles. In one embodiment, the weight average particle diameter is 50 μm to 5000 μm. In another embodiment, a plasticiser is added to the agglomerated PHA particles.

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HOT SHAPING POLYHYDROXYALKANOATE POLYMERS

This invention relates to a method of hot shaping polymers and in particular to such a method characterized by the nature of the polymer feed to the method.

Hot shaping methods include extrusion of melt, melt coating, compression moulding, injection moulding, extrusion blow moulding and casting. A common feature of these methods is that solid polymer powder is fully or locally melted and caused to flow into a shaping space. The particle size of the polymer powder starting material is carefully controlled to avoid dusting and to ensure uniform flow into the shaping machine. For such particle size control it is usual to subject polymer raw material to pre-extrusion to strands about 3 mm thick and to chop the strands into short lengths about 3 mm long. This has the undesirable effect when the polymer is a polyhydroxyalkanoate (PHA) of causing a significant loss in molecular weight. However, the PHA polymer raw material as available from microbiological production is of such a particle size that pre-extrusion is essential.

Co-pending application WO 94/02622 describes a process of agglomerating PHA particles in suspension in water optionally containing at least partly chemically degraded non-PHA microbial cell material (NPCM) by maintaining the suspension at a relatively high temperature, for example over 100°C but at least 30°C below the peak melting point of the PHA (as determined by differential scanning calorimetry). The agglomerates so produced are said to have a weight average diameter of at least 50 μm, preferably 100 to 1000 μm, and the Examples show such diameters of 346, 300 and 250 μm.

GB application 9525932 filed December 16, 1995 discloses a further development of the above process.

It has now been found that the above process and its further development are capable of producing larger agglomerates and that so-produced agglomerates, whether in the range disclosed in the co-pending application or above that range, can be used as feed to a hot shaping method without pre-extrusion.

According to the invention a polymer hot shaping method is characterised by using as feed to the shaping machine a polymer powder made by agglomerating fine polymer particles in presence of hot water.

The invention is more particularly a process of making a shaped object of microbiologically produced PHA by the steps:

(a) forming by fermentation an aqueous biomass of cells containing PHA particles;

(b) separating non-PHA cell material (NPCM) and bringing PHA particles into suspension in water;

(c) agglomerating the suspended PHA particles to a weight average particle diameter in the range required for hot shaping feed;

(d) separating the resulting agglomerates as dry particles; and

(e) hot shaping the resulting dry particles without hot pre-compounding.

The PHA is especially capable of a relatively high level of crystallinity, for example over 30%, especially 50-90%. It typically has units of formula 1:

$$- O - C_mH_n - CO -$$

where m is in the range 1-13 and n is 2m or (except when m is one) 2m-2. Typically C_mH_n contains 2-5 carbon atoms in the polymer chain and the remainder (if any) in a side chain. In very suitable PHAs m is 3 or 4, n is 2m and especially there are units with m = 3 and m = 4 copolymerised together with respectively a C_1 and C_2 side chain on the carbon next to oxygen. Particular PHAs contain a preponderance of m = 3 units, especially with at least 70 mol % of such units, the balance being units in which m = 4. The molecular weight of the polymer is for example over 50000, especially over 100000, up to e.g. 1×10^6.

PHA of formula (1) containing only m = 3 units may be referred to as PHB; and PHA containing m = 3 and m = 4 units is the co-polymer polyhydroxy-butyrate-co-valerate (PHBV). PHBV preferably contains 4-20% of m = 4 units. Since the intended PHA product can be a blend of two or more PHAs differing in the value of m, a corresponding mixture of fermentation products or suspensions can be used in step (c) . A particular example contains:

(a) PHA consisting essentially of Formula 1 units in which 2-5 mol % of units have m = 4, the rest m = 3; and

(b) PHA consisting essentially of Formula 1 units in which 5-30 mol % of units have m = 4, the rest m = 3.

The proportions of the PHAs in such blends are preferably such as given an average m = 4 content in the range 4-20 mol %.

In step (a) the microorganism may lay down PHA during normal growth or may be caused to do so by cultivation in the absence of one or more nutrients necessary for cell multiplication. The microorganism may be wild or mutated or may have had the necessary genetic material introduced into it. Alternatively the necessary genetic material may be harboured by a eukariote, to effect the microbiological process.

Examples of suitable microbiological processes are the following:

for Formula 1 materials with m = 3, or m = partly 3, partly 4: EP-A-69497 (Alcaligenes eutrophus);

for Formula 1 materials with m = 3; US 4101533 (A. eutrophus), EP-A-144017 (A. latus);

for Formula I material with m = 7-13: EP-A-0392687 (various Pseudomonas).

Step (b) typically comprises subjecting the biomass, possibly after concentration, to one or more mechanical steps such as homogenisation, thermal steps such as heat shock at 100-200°C, enzymatic steps such as by proteolytic enzyme or hydrolase such as lysozyme, surfactant digestion, or oxidation such as by peroxide or hypochlorite. Very suitably it is subjected to peroxide, optionally after at least one of the mechanical, thermal or enzymatic steps. The peroxide treatment is preferably by hydrogen peroxide in presence of a metal sequestering agent. One or more surfactants may be present, as an NPCM solubiliser or dispersion stabiliser or for other purposes.

An alternative process for producing the suspension includes extracting the PHA by means of a volatile water-insoluble solvent such as chloroform and emulsifying the resulting solution in water. A further alternative includes melting the PHA out from the cells, possibly in presence of a water-soluble solvent, then shearing the resulting melt or solution with water.

The temperature in step (c) is by 30-80°C, preferably 40-70°C lower than the melting point of the PHA as measured by DSC. Typically the temperature is over 100°C and agglomeration is carried out under superatmospheric pressure. It will be appreciated that the temperature is stated

in terms of the DSC melting point of the PHA because the PHA particles at the time of agglomeration are in transition between the amorphous state and the crystalline state, so that their melting point cannot be known.

Whereas the starting PHA particles are typically of weight average diameter in the range 0.1 to 5 μm, step (c) typically increases this to at least 50, preferably 100-5000, for example 200-500, μm. Their porosity is then typically at least 0.6, especially 0.7 to 0.8, by volume. If desired, polymer processing additives such as nucleant, pigment, filler, plasticiser or additional polymer can be introduced in this step, before, during or after agglomeration. Generally the particles are porous enough to absorb plasticiser to the extent required, for example 5-20 phr by weight.

In step (d) the agglomerates may be separated from the aqueous phase of the suspension by for example decantation, filtration or centrifugation. In any such method there may be one or more steps of resuspension, washing and re-separation, to ensure more complete removal of solubilised NPCM and any surfactant from the agglomerates. It is an advantage of using an agglomeration step that such separation and washing can be effected by decantation and/or filtration, without the expense and complication of enhanced-gravity machinery such as a centrifuge.

In step (e) hot pre-compounding is replaced by simple cold mixing, followed if necessary by drying if a volatile liquid such as water has been used to introduce a component of the material to be shaped. If shaping is to be by screw extrusion, dry mixing may be sufficiently effected in passage through the extruder screw.

Alternatively at least part of the intended additives can have been introduced at step (c).

EXAMPLE

Three samples of PHBV 92:8 molar agglomerates mainly in the range 500-1000 μm:

(a) no addition;

(b) mixed dry with 1 phr w/w of finely divided boron nitride; and

(c) as (b) with also 10 phr w/w of acetyl-tri-n-butyl citrate (ESTAFLEX ATBC);

were separately fed into an extruder with a 40 mm diameter screw. The screw was operated at a speed of 70-180 rpm. The extruder fed into a 20 cm wide die. The temperature of the melt

measured close to the die was 190°C according to a calibrated thermocouple. The molten PHBV was extruded onto 80 g/m^2 SIMCASTOR (RTM) paper in the nip between a first nip-roll and a chill-roll water cooled to 40°C. The gap between the extruder die lips was set to 0.4 mm; the air gap between these lips and the nip was set to about 10cm. The paper line speed was 20-40 m/min. Downstream of the chill-roll, the coated web was heated to approximately 80°C with an infra red heater to crystallise the PHBV. The coating was satisfactory in its appearance and ran smoothly through to the wind-up. The coated paper could be unwound without any difficulties.

These runs were repeated with feed of low density polyethylene film between the PHBV layer and the chill-roll. Again satisfactory uniform PHBV layers were obtained. The polyethylene layer was readily strippable from the PHBV layer.

WHAT IS CLAIMED IS:

1. A process for producing a shaped object of polyhydroxyalkanoate (PHA), comprising: producing a biomass containing particles of PHA and non-PHA cell material (NPCM); separating the NPCM and suspending the PHA particles in water;

agglomerating the suspended PHA particles at a suitable temperature to a suitable weight average particle diameter required for hot shaping feed;

separating the agglomerated PHA particles from the suspension and drying the agglomerated PHA particles; and

hot shaping the dry, agglomerated PHA particles.

2. The process of Claim 1 wherein the temperature of said agglomerating is 30 °C to 80 °C below the melting point of the PHA.

3. The process of Claim 1 wherein the temperature of said agglomerating is 40 °C to 70 °C below the melting point of the PHA.

4. The process of Claim 1 wherein the temperature of said agglomerating is at least 100 °C.

5. The process of Claim 1 wherein the weight average particle diameter is 50 μm to 5000 μm.

6. The process of Claim 1 wherein the weight average particle diameter is 200 μm to 500 μm.

7. The process of Claim 1 further comprising introducing a polymer processing additive to the agglomerated PHA particles.

8. The process of Claim 7 wherein the additive is a plasticiser.

9. The process of Claim 1 wherein said separating comprises oxidizing the NPCM in the presence of a chelator.

10. The process of Claim 1 wherein said separating is conducted in the presence of a surfactant.

11. The process of Claim 1 wherein the PHA consists of repeating units of:

$$- O - C_mH_n - CO -$$

wherein m is between 1 and 13 and n is 2m or 2m-1.

12. The process of Claim 1 wherein the PHA is polyhydroxy-butyrate-co-valerate copolymer.

13. A process for producing a shaped object of microbiologically produced polyhydroxyalkanoate (PHA), comprising:

agglomerating the suspended PHA particles at a suitable temperature to a suitable weight-average particle diameter required for hot shaping feed;

separating the agglomerated PHA particles from the suspension and drying the agglomerated PHA particles; and

hot shaping the dry, agglomerated PHA particles.

14. The process of Claim 13 wherein the temperature of said agglomerating is 30 °C to 80 °C below the melting point of the PHA.

15. The process of Claim 13 wherein the temperature of said agglomerating is 40 °C to 70 °C below the melting point of the PHA.

16. The process of Claim 13 wherein the temperature of said agglomerating is at least 100 °C.

17. The process of Claim 13 wherein the weight average particle diameter is 50 μm to 5000 μm.

18. The process of Claim 13 wherein the weight average particle diameter is 200 μm to 500 μm.

19. The process of Claim 13 further comprising introducing a polymer processing additive to the agglomerated PHA particles.

20. The process of Claim 19 wherein the additive is a plasticiser.

21. The process of Claim 13 wherein the PHA consists of repeating units of:

$$- O - C_mH_n - CO -$$

wherein m is between 1 and 13 and n is 2m or 2m-1.

22. The process of Claim 13 wherein the PHA is polyhydroxy-butyrate-co-valerate copolymer.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 96/20545

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08J3/12 C08J5/00 //C08L67:04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08J C12P

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	WO 94 02622 A (ZENECA LIMITED) 3 February 1994 cited in the application see claims 1-5 see examples 1-3 see page 2, line 26 - page 3, line 7 see page 6, line 20-25 ---	1-6, 11-18, 21,22 1,7,8, 13,19,20
Y	WO 94 07940 A (ZENECA LIMITED) 14 April 1994 see claims 1,5,7-9,11 see page 4, line 28 - page 5, line 18 ---	1,7,8, 13,19,20
A	WO 94 24302 A (ZENECA LIMITED) 27 October 1994 see claim 1 --- -/--	1,9

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[X] Patent family members are listed in annex.

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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Information on patent family members

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